Eco-Friendly Boron Complex Addition to Aldehydes

A THESIS SUBMITTED TO THE FACULTY OF THE UNIVERSITY OF MINNESOTA BY:

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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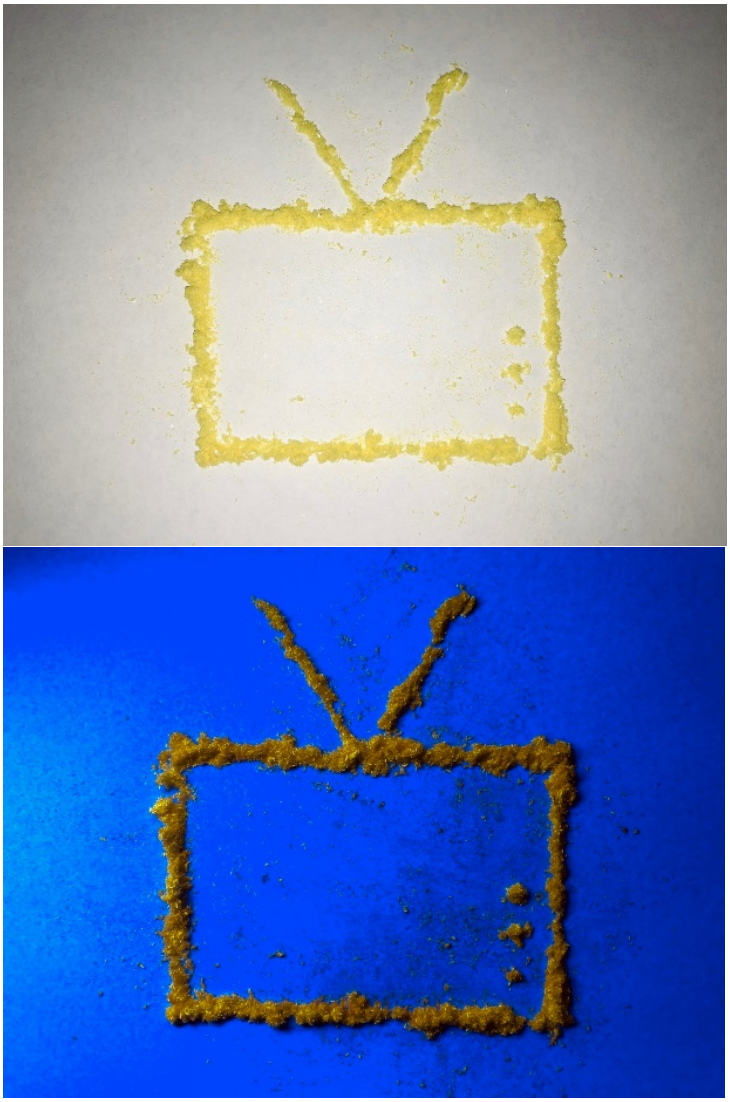
August 2019

ABSTRACT

A series of aldehyde ligands were synthesized to increase yield and decrease resource use and waste production. Boron diphenyl complexes were then separately added to each of the ligands greatly increasing and shifting their intensity and fluorescence wavelength. The complexes were characterized via NMR and GCMS. The stability of these luminescent boron complexes and ability to be vacuum sublimated onto a glass surface makes them suitable for OLED application.



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CHAPTER 1: INTRODUCTION AND BACKGROUND-

MICROSCALE APPROACH TO KEEPING EXPLORATORY SYNTHESIS "GREEN"

With the constant drive for scientific evolution, its pace is hindered not by a lack of creativity or ingenuity, but by time, resources, and funds. A new method or synthesis may seem promising, but after a two-day reflux, vacuum filtration, recrystallization, NMR, and GCMS, inadequate results can swiftly become detrimental. A 25-gram supply of starting material could be depleted after just a few dozen failed reactions. With small jars of starting materials costing from $70-$300, synthesis by trial-and-error can end before concrete results are obtained or dry up the group's funds, inhibiting future discoveries. Hazardous waste is generated quickly by failed reactions or experiments. Solvents are used in large amounts just to be rotary vacuumed off. In the short span of two years, without neglecting sleep, social life, and family, only a limited number of attempts can be made to discover a new structure, chemical, or synthetic route. Every attempt drains time, resources, and funds. Every failure lessens the percentage of success. As a researcher, "publish or perish" may ring true as yet another experiment is poured into the waste bottle; however, coupling the experimental procedures need's with an eco-friendly view can greatly increase the chances of success.

Microscale synthesis is covered in most organic chemistry labs and its use to minimize resources is well known. By substituting pipet column chromatography for the standard size columns[18], microwave irradiation[22] or traditional stirring and heating for refluxes[17], an experiment can develop into an efficient, time and resource saving process. For the synthesis of Ligand 5, running just 10 reflux reactions would take nearly a month and cost over $300.00 for materials alone. With the refined microscale method, running 10 microwave reactions and the necessary purification, it cost under $10.00 and could be completed in 3 days. A stirring and heating until dissolved method could be completed in a single day. The second two options are far more ideal in the beginning stages of research chemistry.

The scale-down process starts with the reactants being scaled down to 0.050-0.100g. This can be paired with 10 mL glassware and 4-8 mL of solvent. The goal is to produce just slightly over the amount that would be needed to run all verification tests. It has been found that between 50-70 mg of product is plenty for an NMR, GCMS, and Fluorimeter with product left over. The leftover product is minimal, so that after a project has been completed only a miniscule amount of waste is produced. This concept is very easy to apply to most 1-2 step syntheses. The amount would have to be increased slightly for two-step reactions, as has been done for the boron complexes 1-5. Reactions requiring more than 3 steps are not ideal for microscale research; however, the effort instead, can be put into reducing the number of steps needed.

Solvent reduction plays a large role in achieving “green” chemistry. Solvents make their way into hazardous waste containers quickly after a reaction. They can be saved as mixed solvent for cleaning glassware before the base bath; however, for environmental reasons it is best to limit their use in the first place. New solvent-free methods are emerging such as grinding and mixing in the solid state, but the exact reaction pathways are not always well known. By keeping reactions at microscale level, less solvent waste is generated, and less glassware surface area must be cleaned afterwards. Each reaction uses 2-4 mL of solvent and an additional 2 mL for washing. This solvent is saved in a mixed solvents waste and gains an additional use as a glassware cleaner before it is finally disposed of as hazardous waste. OSHA lists many solvents as toxic to the nervous system, reproductive system, liver, kidneys, respiratory system, and could lead to cancer or dermatitis. Large amounts of solvent can generate ground-level ozone, when in contact with sunlight, creating problems for organic life and compromising building materials. Due to these factors, it would be environmentally sound to generate as little solvent waste as possible.

Energy use can also be slightly reduced. Two previously published ligands both utilize 7-24 hour refluxes[11,27]. This is a fair amount of energy output for the stir and hotplate. Water is also constantly running through the condenser column. By microwaving the reactions for 10 min this energy need is decreased. Some of the complexes can even be taken a step further, due to kinetics, and be stirred in a hot water bath until the reactants dissolve (~5 minutes). This method works

best when the reactants are added together in suspension or solution, depending on their solubility in isopropanol.

OLED POTENTIAL OF DIPHENYLBORON COMPLEXES

The commonality of organic light emitting diodes (OLEDs) has greatly increased in daily life[29]. The basis of OLED structure is a ligand coordinated to a metal center; however, it is also found that organic material can replace the ligand or semi-metal fragments can replace the metal center. A common metal used instead of semi-metal boron is aluminum[2]. Copper, zinc, beryllium, and lithium have also been utilized as OLED metal centers[12]. Boron has made its way into fluorescent materials[20, 31], cellular imaging[15], and dyes[11], amongst other applications.

Evolution of technology has recently turned in favor of OLED (organic light emitting diodes) applications. OLED screens are thinner, self-illuminated, and can be manufactured with a curved shape. Compounds with tunable fluorescence, and the ability to be vacuum sublimated onto a glass surface are desirable for OLED application. The emission of light gives OLED screens their true blacks and incredible vivid and crisp pictures compared with LCD displays. OLED lights decrease in size and product needed for production, without compromising brightness or quality[23,29].

Boron bonds stably between nitrogen/oxygen and nitrogen/nitrogen on ligands. Many ligands are quenched via excited state intermolecular proton transfer (ESIPT); therefore, the boron diphenyl addition disturbs this process and the fluorescence increases. The N-B dative bond is necessary for the fluorescent activity and properties[12]. Boron can bind between two nitrogen or an oxygen and nitrogen with the known possible attachments of two phenyls, alkyls, fluoros, aryls, and a few others[6,8]. Boron difluoro addition[24-25] appears to be the most commonly explored complex addition. Boron diphenyl addition[12, 16]; however, appears to be a viable and less hazardous option.

A variety of substituted ligands were synthesized, chosen for their tunability and a donor nitrogen atom in addition to a hydroxy group (OH). The aromatic hydroxy group can form an ester with a boron diphenyl fragment, that would be added later. The nitrogen atom serves as a donor atom to complete the octet of boron. With both, the oxygen through a covalent bond and the nitrogen with a dative bond attached to boron, the coordination is stable and makes the compounds good candidates for OLED applications. The boron diphenyl addition is completed by vacuum sublimation onto a cold finger to remove volatiles[12]. This ability further makes them OLED desirable.

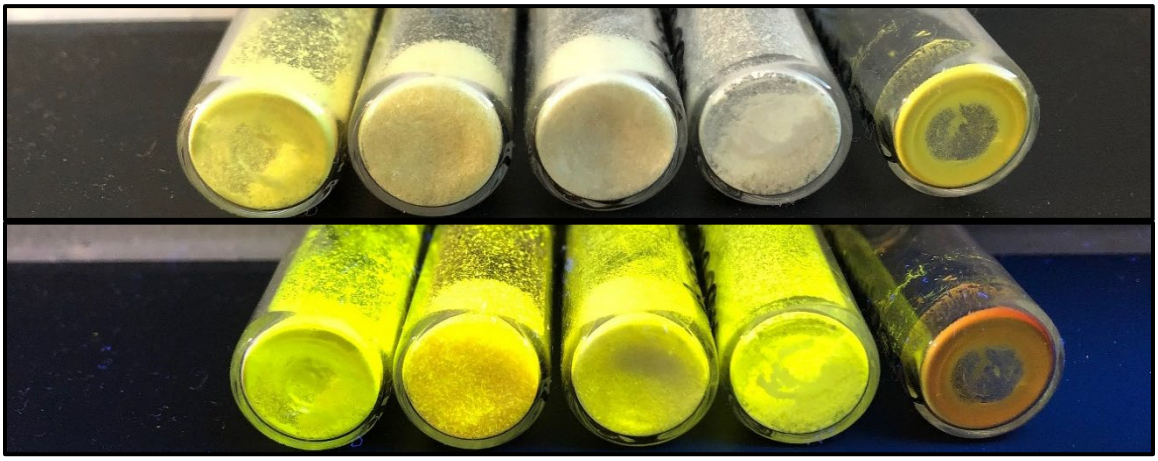
CHAPTER 2:
RESULTS AND DISCUSSION-

BORON COMPLEX ADDITION FOR POTENTIAL OLED USE

The addition of boron diphenyl fragments to ligands has been successfully published. The published method of synthesis via reflux consumes 7-24 hours of lab time, water usage, and required larger amounts of the reactants. Using microwave irradiation to decrease time and materials, produces an undesirable minor product. Stirring in a hot water bath at 100 °C until dissolved (5 min.) then cooling, produced the purer and higher yield products. The five aldehyde ligands were chosen for their N/OH proximity, giving the boron fragment a site for addition by removing the H and binding between the N and O stably. The boron diphenyl addition gave an increase in fluorescent intensity and shifted its current emission wavelength. This is due to the ESIPT (excited state internal proton transfer) from the O to the N. A ferrocene ligand was synthesized; however, it exhibits quenching due to the electron donating ferrocene making it a poor choice for this study. Two ligands were chosen from previous papers to provide a baseline (Ligands 1 and 3) and the other three were chosen to provide a variety of tunability (Ligands 2, 4, and 5). Ligand 2 was expended to have similar fluorescence data to ligand 1 and ligand 4 to ligand 3. Ligand 5 was chosen as it

provides variety, being a yellow solid that fluoresces orange not yellow, as the other ligands do.

Figure 1. Ligands 1-5 in natural light vs UV light
Ligands 1 and 2 and ligands 3 and 4, exhibit similar fluorescent properties as confirmed via the Varian Cary Eclipse Fluorometer. Ligand 5 is unique as it fluoresces orange under UV.



The method of synthesizing the ligands remained consistent even with a change in aldehyde R-group from ligand to ligand. Salicylaldehyde hydrazone was suspended in 3 mL isopropanol, the chosen aldehyde (2:1 aldehyde to salicylaldehyde hydrazone ratio) was dissolved/suspended in 5 mL isopropanol and the salicylaldehyde suspension was added dropwise while stirring in a hot water bath. The vial was then chilled. The resulting solid was filtered and washed with isopropanol. The solid was then confirmed through GCMS and NMR. Fluorescence emission and excitation data were also obtained.

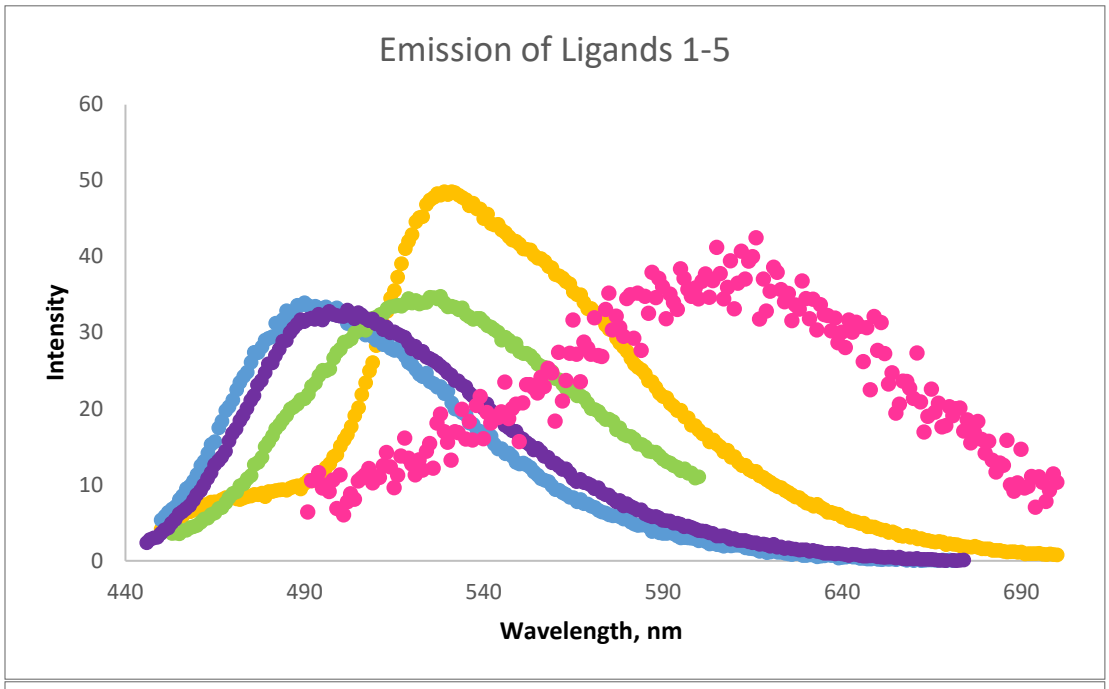
The ligands were added to freshly prepared borinic acid and refluxed using a microscale setup with a Dean Stark trap for an hour to remove the water. The resulting sticky product was vacuum sublimated to remove volatiles. The

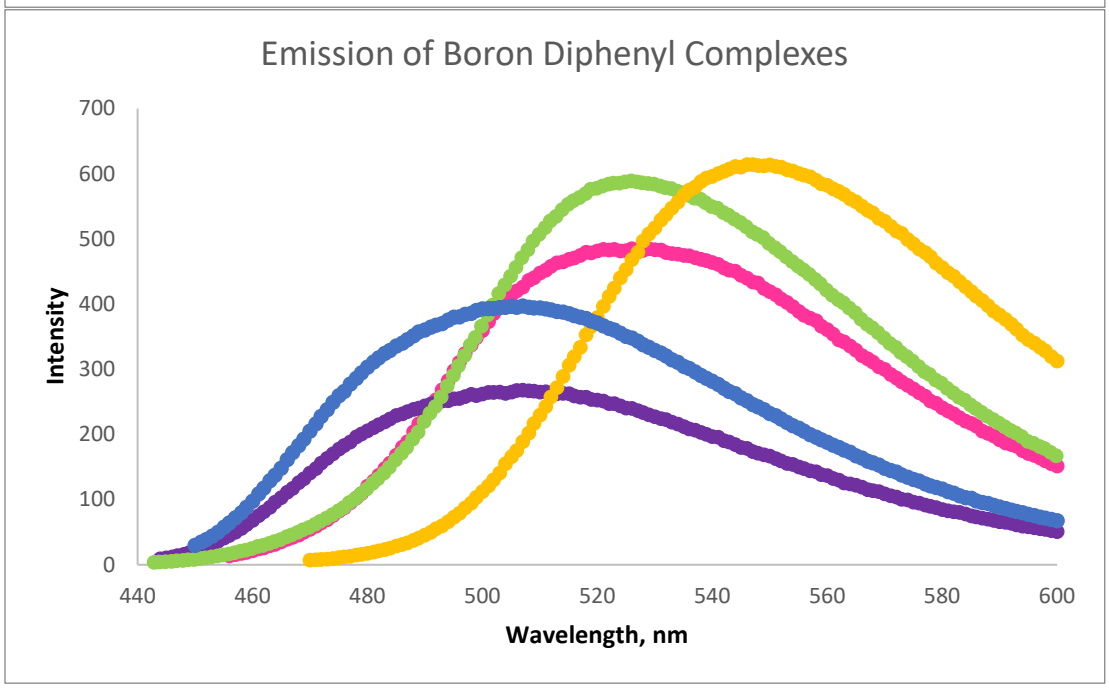
solid was verified through NMR. Fluorescence emission and excitation data was obtained. Due to the boron diphenyl fragment a large intensity increase and a minor shift in emission wavelength was seen from its previous ligand.

The choosing of a synthesis method started as the previously published reflux of ligands 1 and 3. Due to the known success of reflux reactions to microwave irradiations, the ligands were irradiated producing high levels of the minor product, salicylaldehyde azine. Pipet columns were attempted to keep the synthesis microscale, but the major and minor products were too similar and eluded together. A published ferrocene ligand was produced by stirring over night resulting in high yields without reflux. This concept was applied to the chosen ligands, but the ferrocene ligand was abandoned due to its quenched fluorescence. The ligands were then added dropwise and stirred. To aid in the speed of the reaction, the solution was heated lightly (100°C) until the reactants dissolved, ~5 minutes. The reaction vial was then removed from the hot water bath and the product immediately began precipitating out. To be cautious, the vial was cooled in the refrigerator to ensure all the product could be filtered and washed.

A convenient aspect of the chosen ligands is their fluorescence under UV light. To further the goal of saving time and resources, the dried product under UV light would visually show the presence of high or low levels of impurity. The undesired minor product, salicylaldehyde azine, fluoresces an incredibly strong yellow. The ligands themselves fluoresce in a range of a less intense yellow to orange. To prevent unnecessary GCMS or NMR runs, if the product was visually

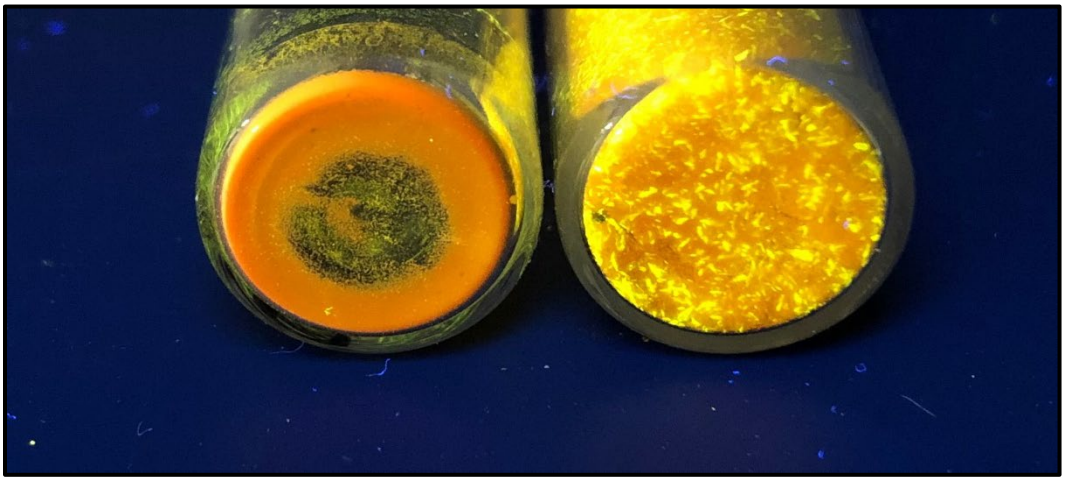
Figure 2. Emission Wavelength Variety of Boron Diphenyl Complexes
The change in emission wavelength and intensity range due to the addition of a boron diphenyl fragment. Intensity varies amongst ligands and complexes due to the amount of sample used, therefore cannot be relevant. [Key: Ligand 1 (orange), Ligand 2 (purple), Ligand 3 (blue), Ligand 4 (green), and Ligand 5 (pink).]





high in salicylaldehyde content, the sample was discarded, and a new method was developed.

Figure 3. Microwave Irradiation vs Stir and Heat until Dissolved under UV Samples of ligand 5 synthesized via Stir and Heat until Dissolved (left) and Microwave Irradiation (right). It can be visually observed under UV light that a high concentration of salicylaldehyde is present (bright yellow).



Ligands 1 and 3 were compared to previously published NMR data to ensure that the methods were still producing the same products. The ^{1}H NMR peaks for ligand 1 match up, which the exception of a published doublet and triplet being observed as a multiplet. No ^{13}C NMR data was published. The published peaks for Ligand 3; however, pose a few questions. A distinct and expected O-H peak around 11 ppm, due to hydrogen bonding, was not present in the published NMR data. The ligand synthesized via an alternative method showed salicylaldehyde contamination in the aromatic peaks, but the O-H peak was observed. No ^{13}C NMR data was published.

Table 1. ^{1}H NMR Data of Ligand 1 Alternate Synthesis Compared to Published Reflux

Ligand 1 was synthesized via a Stir and Heat until Dissolved method verse the previously published method in Dyes and Pigments of a 2-step, 7 hour reflux followed by a chromatography column.[1]

1. Published, ^{1}H	1. Experimental, ^{1}H	1. Experimental, ^{13}C
11.53, s, 1H	11.97, s, 1H	162.66
8.85, s, 1H	8.72, s, 1H	162.53
8.60, s, 1H	8.52, s, 1H	159.63
7.68, d, 1H, J= 8.36 Hz	7.71, d, 2H, J= 9.0 Hz	152.62
7.58,d, 1H, J= 7.84 Hz	7.43-7.30, m, 2H	132.14
7.33, t, 1H, J= 7.56 Hz		131.91
6.92-6.98, m, 2H	7.06-6.90, m, 2H	130.43
6.76, d, 2H, J= 8.32 Hz	6.73, d, 2H, J= 9.0 Hz	121.03
3.00, s, 6H	3.00, s, 6H	119.30
		118.21
C: 71.89	*LCMS unavailable at UMD at this time*	116.83
H: 6.41		111.67
N: 15.72		47.58
Yield: 77%	**Yield: 65%** (20% salicylaldehyde azine)	40.13

Table 2. ^{1}H NMR Data of Ligand 3 Alternate Synthesis Compared to Published Reflux

Ligand 3 was synthesized via a Stir and Heat until Dissolved method verse the previously published method in Inorganic Chemistry of a 2-step, 1-day reflux.[3]

3. Published, ^{1}H	3. Experimental, ^{1}H	3. Experimental, ^{13}C
****missing OH*	11.67, s, 1H (OH)	165.49
8.59, s, 2H (C=N)	8.77, s, 1H (C=N)	164.75
	8.59, s, 1H (C=N)	160.96
7.79, d, 2H, J= 8.0 Hz	7.79, d, 2H, J= 8.5 Hz	159.92
7.45, d, 2H, J= 8.0 Hz	7.44, d, 2H, J= 8.5 Hz	133.48
7.38-7.34, m, 2H	7.37, m 4H	133.16
	7.04, m, 2H	132.48
7.05-6.92, m, 2H	6.96, t, 1H, J= 7.5 Hz	132.12
		129.83
		129.25
		119.58
= 64% yield	**= 40% yield** (50% salicylaldehyde azine)	117.08

The inconsistency shows between the two published ligand methods. Published ligand 1 required a chromatography column and a 7 hour reflux.[1] Published ligand 3 required no additional purification and a 24 hour reflux, but showed an absence of the O-H peak.[3] This makes choosing a method difficult. The

publication of ligand 1 seems sounder, as the disappearance of the O-H peak is vital in confirming the boron diphenyl addition. The high level of minor product seen in microwaved samples verse Stir and Heat until Dissolved samples is also confusing as, according to published ligand 3 procedure, a longer reflux removed the need for further purification.[3] This was not observed in the alternate synthesis of ligand 3.

Table 3. Method vs Purity and Yield Results
Microwave Irradiation was run at 150°C for 10 minutes. The Stir and Heat until Dissolved Method applied low heat (100°C) until the solid reactants dissolved (~5 minutes). The yield percentages do not include the salicylaldehyde azine present (ex. 90% yield with 50% salicylaldehyde azine = 45% yield).

	CEM Discover Microwave Yield	CEM Discover Microwave Purity	Stir and Heat until Dissolved Yield	Stir and Heat until Dissolved Purity
Ligand 1	40%	~50% salicylaldehyde azine	65%	20% salicylaldehyde azine
Ligand 2	45%	~50% salicylaldehyde azine	58%	20% salicylaldehyde azine
Ligand 3	35%	~60% salicylaldehyde azine	40%	50% salicylaldehyde azine
Ligand 4	31%	~50% salicylaldehyde azine	45%	38% salicylaldehyde azine
Ligand 5	49%	~50% salicylaldehyde azine	75%	0% salicylaldehyde azine

Percentage of the contamination minor product, salicylaldehyde azine, was determined via GCMS for the microwave irradiation method and via NMR for

the stir and heat until dissolved method. GCMS and NMR graphs show the area of the salicylaldehyde peak and the ligand peak. These can be integrated to yield a percentage. The NMR peaks relied on the O-H peak of the ligand to compare to the slightly less upshifted peak of the salicylaldehyde azine. Due to the NMR being demeaned far for exact than the GCMS, the percentages from the GCMS were therefore approximate.

CHAPTER 3: EXPERIMENTAL SYNTHESIS-PROCEDURES AND ANALYSIS

Microwave irradiation was performed using a CEM Discover Benchmate. Mass spectra was recorded on an Agilent Technologies GCMS with triple-axis detector. ^{1}H and ^{12}C NMR were obtained on an Oxford 500 MHz NMR. Fluorescence was measured on a Varian Cary Eclipse fluorescence spectrophotometer. Chemicals were purchased from Acros Organics, MP Biomedial LLC, Alfa Aesar, Beantown Chemical, Aldrich, Ark Farm Inc.,Sigma, and Accela. All solvents were ACS grade and required no further drying or purification. Ligand percent yields account for salicylaldehyde azine present and only represent pure product present. Boron Complex yields do not account for salicylaldehyde azine present and represent impure product.

Ligand 1:

2-((E)-((E)-(4-(dimethylamino)benzylidene)hydrazono)methyl)phenol

In a 10mL vial, 4-dimethylaminobenzaldehyde (0.284g, 1.90 mmol) was dissolved in 3 mL of isopropanol. The vial was placed in a hot water bath and stirred with a micro stir bar until fully dissolved. Salicylaldehyde hydrazone (0.136g, 0.99 mmol) was added to a separate vial with 5 mL of isopropanol. Using a pipet, the salicylaldehyde hydrazone solution was added dropwise to the 4-dimethylaminobenzaldehyde solution and stirred in the hot water bath until fully dissolved. The vial was then removed from the hot water bath, allowing the

product to crystalize. The resulting bright yellow needle-like crystals were filtered and washed in isopropanol. Yield: 0.217g (65%) ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.97 (s,1H, O-H); 8.72 (s, 1H, H-C=N); 8.52 (s,1H, H-C=N); 7.71 (d, J= 9.0 Hz, 2H); 7.43-7.30 (m, 2H); 7.06-6.90 (m, 2H); 6.73 (d, J= 9.0 Hz, 2H); 3.06 (s, 6H, CH_3). ^{13}C NMR (500 MHz, $CDCl_3$) : δ (ppm) = 162.66, 162.53, 159.63, 152.62, 132.14, 131.91, 130.43, 121.03, 119.30, 118.21, 116.83, 111.67, 47.58, 40.13.

Ligand 2: 2-((E)-((E)-(4-cyanobenzylidene)hydrazono)methyl)phenol

In a 10mL vial, 4-cyanobenzaldehyde (0.023g, 0.175 mmol) was dissolved in 3 mL of isopropanol. The vial was placed in a hot water bath and stirred with a micro stir bar until fully dissolved. Salicylaldehyde hydrazone (0.021g, 0.147 mmol) was added to a separate vial with 5 mL of isopropanol. Using a pipet, the salicylaldehyde hydrazone solution was added dropwise to the 4-cyanobenzaldehyde solution and stirred in the hot water bath until fully dissolved. The vial was then removed from the hot water bath, allowing the product to crystalize. The resulting bright-yellow needle-like crystals were filtered and washed in isopropanol. Yield: 0.033g (58%) ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.54 (s, 1H, O-H); 8.80 (s, 1H, H-C=N); 8.63 (s, 1H, H-C=N); 7.95 (d, 2H, J= 8.5 Hz); 7.75 (d, 2H, J= 8.5 Hz); 7.42-7.35 (m, 2H); 7.04 (d, 1H, J= 8.5 Hz); 6.98 (t, 1H, J= 7.5 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) : δ (ppm) = 166.78, 164.73, 160.04, 133.66, 133.46, 132.76, 132.60, 132.57, 128.95, 119.75, 119.71, 117.19, 117.17.

Ligand 3: 2-((E)-((E)-(4-chlorobenzylidene)hydrazono)methyl)phenol

In a 10mL vial, 4-chlorobenzaldehyde (0.198g, 1.409 mmol) was dissolved in 3 mL of isopropanol. The vial was placed in a hot water bath and stirred with a micro stir bar until fully dissolved. Salicylaldehyde hydrazone (0.080g, 0.588 mmol) was added to a separate vial with 5 mL of isopropanol. Using a pipet, the salicylaldehyde hydrazone solution was added dropwise to the 4-chlorobenzaldehyde solution and stirred in the hot water bath until fully dissolved. The vial was then removed from the hot water bath, allowing the product to crystalize. The resulting pale-yellow needle-like crystals were filtered and washed in isopropanol. Yield: 0.122g (40%) ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.67 (s, 1H, O-H); 8.77 (s, 1H, H-C=N); 8.59 (s, 1H, H-C=N); 7.79 (d, 2H, J= 8.5 Hz); 7.44 (d, 2H, J= 8.5 Hz); 7.37 (m, 4H); 7.04 (m, 1H); 6.96 (t, 1H, J= 7.5 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) : δ (ppm) = 165.49, 164.75, 160.96, 159.92, 133.48, 133.16, 132.48, 132.12, 129.83, 129.25, 119.58, 117.08.

Ligand 4: 2-((E)-((E)-(4-bromobenzylidene)hydrazono)methyl)phenol

In a 10mL vial, 4-bromobenzaldehyde (0.055g, 0.297 mmol) was dissolved in 3 mL of isopropanol. The vial was placed in a hot water bath and stirred with a micro stir bar until fully dissolved. Salicylaldehyde hydrazone (0.020g, 0.147 mmol) was added to a separate vial with 5 mL of isopropanol. Using a pipet, the salicylaldehyde hydrazone solution was added dropwise to the 4-

bromobenzaldehyde solution and stirred in the hot water bath until fully dissolved. The vial was then removed from the hot water bath, allowing the product to crystalize. The resulting pale-yellow needle-like crystals were filtered and washed in isopropanol. Yield: 0.041g (62%) ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.66 (s, 1H, O-H); 8.77 (s, 1H, H-C=N); 8.57 (s,1H, H-C=N); 7.71 (d, 2H, J= 7.5 Hz); 7.60 (d, 2H, J= 7.5 Hz); 7.37 (m, 2H), 7.00 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 165.53, 164.72, 161.05, 159.91, 133.45, 133.16, 132.56, 132.49, 132.19, 132.12, 129.99, 129.94, 119.57, 117.07.

Ligand 5: 2-((E)-((E)-(4-nitrobenzylidene)hydrazono)methyl)phenol

In a 10mL vial, 4-nitrobenzaldehyde (0.182g, 0.120 mmol) was dissolved in 3 mL of isopropanol. The vial was placed in a hot water bath and stirred with a micro stir bar until fully dissolved. Salicylaldehyde hydrazone (0.200g, 1.469 mmol) was added to a separate vial with 5 mL of isopropanol. Using a pipet, the salicylaldehyde hydrazone solution was added dropwise to the 4-nitrobenzaldehyde solution and stirred in the hot water bath until fully dissolved. The vial was then removed from the hot water bath, allowing the product to crystalize. The resulting bright-yellow needle-like crystals were filtered and washed in isopropanol. Yield: 0.505g (75%) ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.53 (s, 1H, O-H); 8.83 (s, 1H, H-C=N); 8.69 (s, 1H, H-C=N); 8.32 (d, 2H, J= 8.5 Hz); 8.02 (d, 2H, J= 8.5 Hz); 7.40 (m, 2H); 7.04 (d, 1H, J= 8.0 Hz); 6.98 (t, 1H, J= 7.25 Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 167.07, 164.73, 160.15,

159.58, 139.43, 133.77, 133.45, 132.82, 132.58, 129.27, 124.10, 119.75, 117.31, 117.22.

Boron Complex 1: (E)-3-(((dimethylamino)benzyladiene)amino)-2,2-diphenyl-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide

In a 5 mL microscale round bottom flask, ligand **1** (0.008 g, 0.030 mmol) was added with a micro-stirbar. Borinic acid was prepared fresh by dissolving 2-aminoethyl diphenylborinate (0.018 g, 0.080 mmol) in 3 mL of hot ethanol. One drop of concentrated HCl was added, then 2 mL of DI water. 3 mL of toluene was added and the top layer (borinic acid) was extracted and added to the flask containing ligand **1**. The solution was microscale refluxed with a dean stark trap for 1 hour. The resulting sticky orange product was vacuum sublimated to remove volatiles yielding a bright yellow powder. Yield: 0.004g (31%). ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = peaks not reported due to impurity.

Boron Complex 2: (E)-3-(((4-cyanobenzyladene)amino)-2,2-diphenyl-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide

In a 5 mL microscale round bottom flask, ligand **2** (0.047 g, 0.189 mmol) was added with a micro-stirbar. Borinic acid was prepared fresh by dissolving 2-aminoethyl diphenylborinate (0.018 g, 0.080 mmol) in 3 mL of hot ethanol. One drop of concentrated HCl was added, then 2 mL of DI water. 3 mL of toluene was added and the top layer (borinic acid) was extracted and added to the flask containing ligand **2**. The solution was microscale refluxed with a dean stark trap

for 1 hour. The resulting sticky orange product was vacuum sublimated to remove volatiles yielding a bright yellow powder. Yield: 0.002g (3%). ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = peaks not reported due to impurity.

Boron Complex 3: (E)-3-(((4-chlorobenzyladene)amino)-2,2-diphenyl-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide

In a 5 mL microscale round bottom flask, ligand **3** (0.027 g, 0.104 mmol) was added with a micro-stirbar. Borinic acid was prepared fresh by dissolving 2-aminoethyl diphenylborinate (0.018 g, 0.080 mmol) in 3 mL of hot ethanol. One drop of concentrated HCl was added, then 2 mL of DI water. 3 mL of toluene was added and the top layer (borinic acid) was extracted and added to the flask containing ligand **3**. The solution was microscale refluxed with a dean stark trap for 1 hour. The resulting sticky orange product was vacuum sublimated to remove volatiles yielding a bright yellow powder. Yield: 0.010g (23%). ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = peaks not reported due to impurity.

Boron Complex 4: (E)-3-(((4-bromobenzyladene)amino)-2,2-diphenyl-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide

In a 5 mL microscale round bottom flask, ligand **4** (0.034 g, 0.112 mmol) was added with a micro-stirbar. Borinic acid was prepared fresh by dissolving 2-aminoethyl diphenylborinate (0.018 g, 0.080 mmol) in 3 mL of hot ethanol. One drop of concentrated HCl was added, then 2 mL of DI water. 3 mL of toluene was added and the top layer (borinic acid) was extracted and added to the flask

containing ligand **4**. The solution was microscale refluxed with a dean stark trap for 1 hour. The resulting sticky orange product was vacuum sublimated to remove volatiles yielding a bright yellow powder. Yield: 0.004g (8%). ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = peaks not reported due to impurity.

Boron Complex 5: (E)-3-(((4-nitrobenzyladene)amino)-2,2-diphenyl-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide

In a 5 mL microscale round bottom flask, ligand **5** (0.005 g, 0.019 mmol) was added with a micro-stirbar. Borinic acid was prepared fresh by dissolving 2-aminoethyl diphenylborinate (0.018 g, 0.080 mmol) in 3 mL of hot ethanol. One drop of concentrated HCl was added, then 2 mL of DI water. 3 mL of toluene was added and the top layer (borinic acid) was extracted and added to the flask containing ligand **5**. The solution was microscale refluxed with a dean stark trap for 1 hour. The resulting sticky orange product was vacuum sublimated to remove volatiles yielding a bright yellow powder. Yield: 0.006g (74%). ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = peaks not reported due to impurity.

CHAPTER 4:
SUPPLEMENTARY DATA

Figure 1a. GCMS Data of Ligand 1
GCMS Data shows a molecular weight of 267 g/mol as expected for Ligand 1. This agrees with its expected splitting pattern as well.

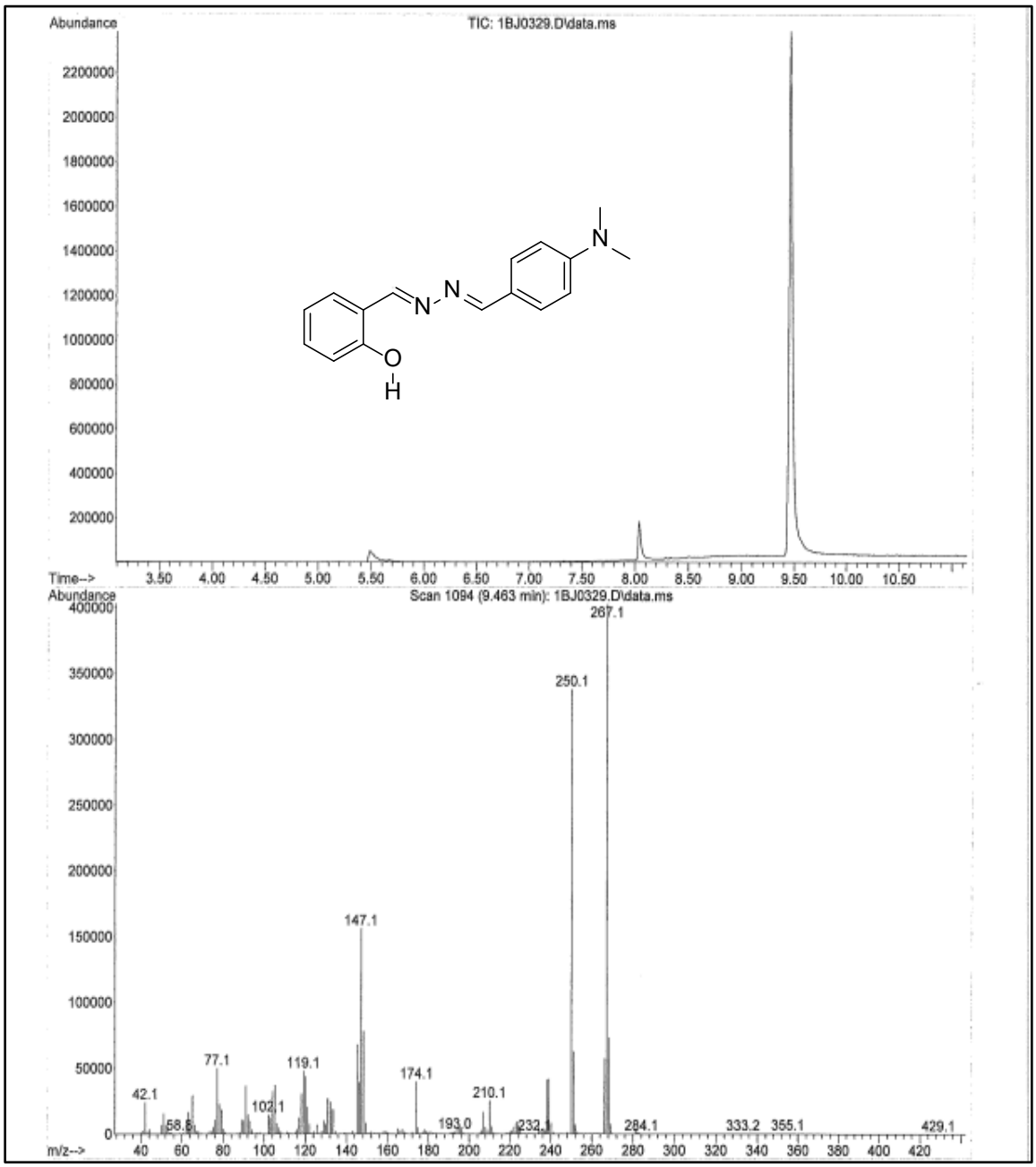


Figure 1b. ^{1}H and ^{13}C NMR of Ligand 1

^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.97 (s,1H, O-H); 8.72 (s, 1H, H-C=N); 8.52 (s,1H, H-C=N); 7.71 (d, J= 9.0 Hz, 2H); 7.43-7.30 (m, 2H); 7.06-6.90 (m, 2H); 6.73 (d, J= 9.0 Hz, 2H); 3.06 (s, 6H, CH_3). ^{13}C NMR (500 MHz, $CDCl_3$) : δ (ppm) = 162.66, 162.53, 159.63, 152.62, 132.14, 131.91, 130.43, 121.03, 119.30, 118.21, 116.83, 111.67, 47.58, 40.13.

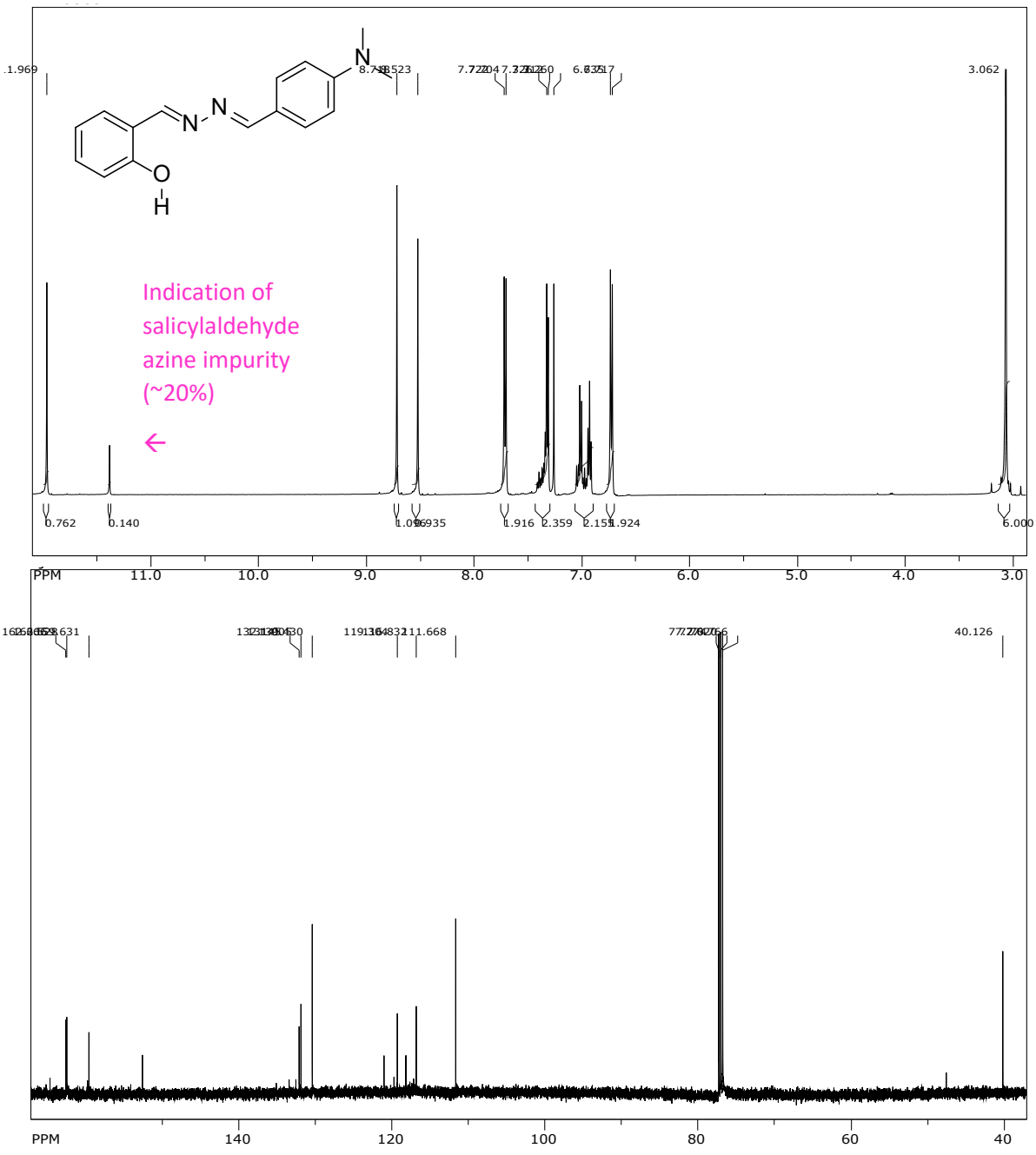


Figure 1c. Cary Fluorometer Data of Ligand 1 and Boron Complex 1

The Boron Complex 1 Intensity is recorded as is from a 5 mg sample in Ethyl Acetate in a quartz cuvette (grey). The Ligand 1 Intensity is shown x10 its actual value from a 5 mg sample in Ethyl Acetate in a quartz cuvette, so the wavelength shift could be seen in the graph (pink). Ligand 1 was excited at 435 nm, giving an emission wavelength of 529 nm. The max intensity was 48.5. Boron Complex 1 was excited at 449 nm, giving an emission wavelength of 547 nm. The max intensity was 612.7. This shows an 18 nm shift and an intensity increase by x12.6.

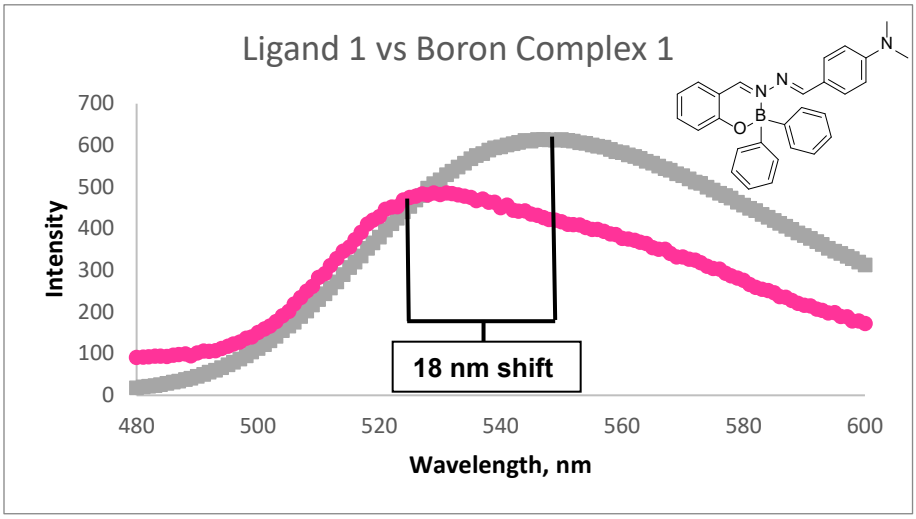


Figure 1d. ^{1}H NMR of Boron Complex 1.

The ^{1}H NMR peaks are not reported as the sample is not yet pure. It can be inferred that residual salicylaldehyde azine was present and a single boron diphenyl attached leaving the other -OH to persist at 11.53 ppm. The aromatic region indicts many impurities; however, it also is a likely sign of the boron diphenyl successfully attaching to the ligand.

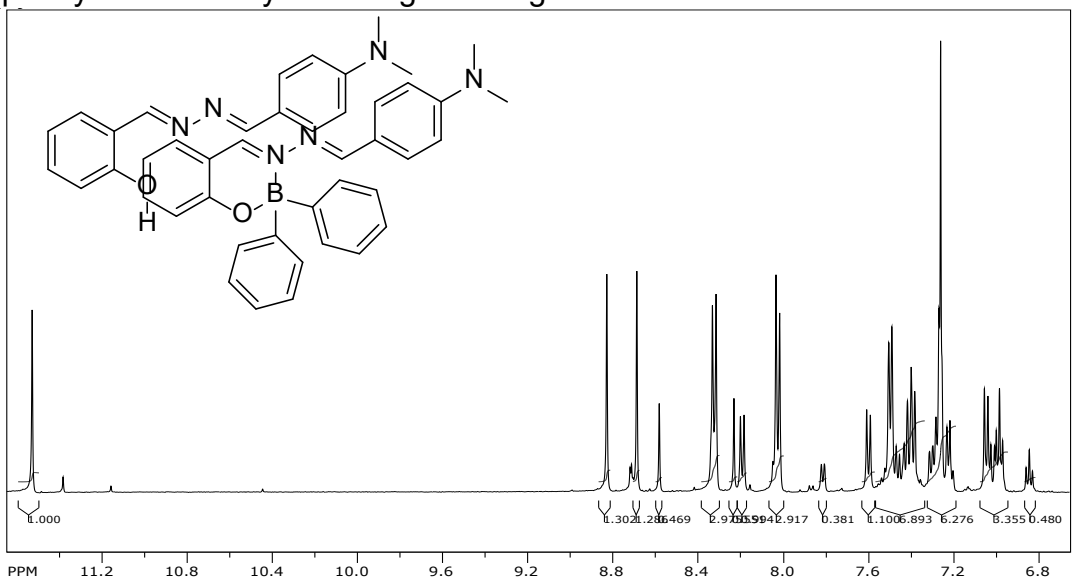


Figure 2a. GCMS Data of Ligand 2

GCMS Data shows a molecular weight of 249 g/mol as expected for Ligand 2. This agrees with its expected splitting pattern as well.

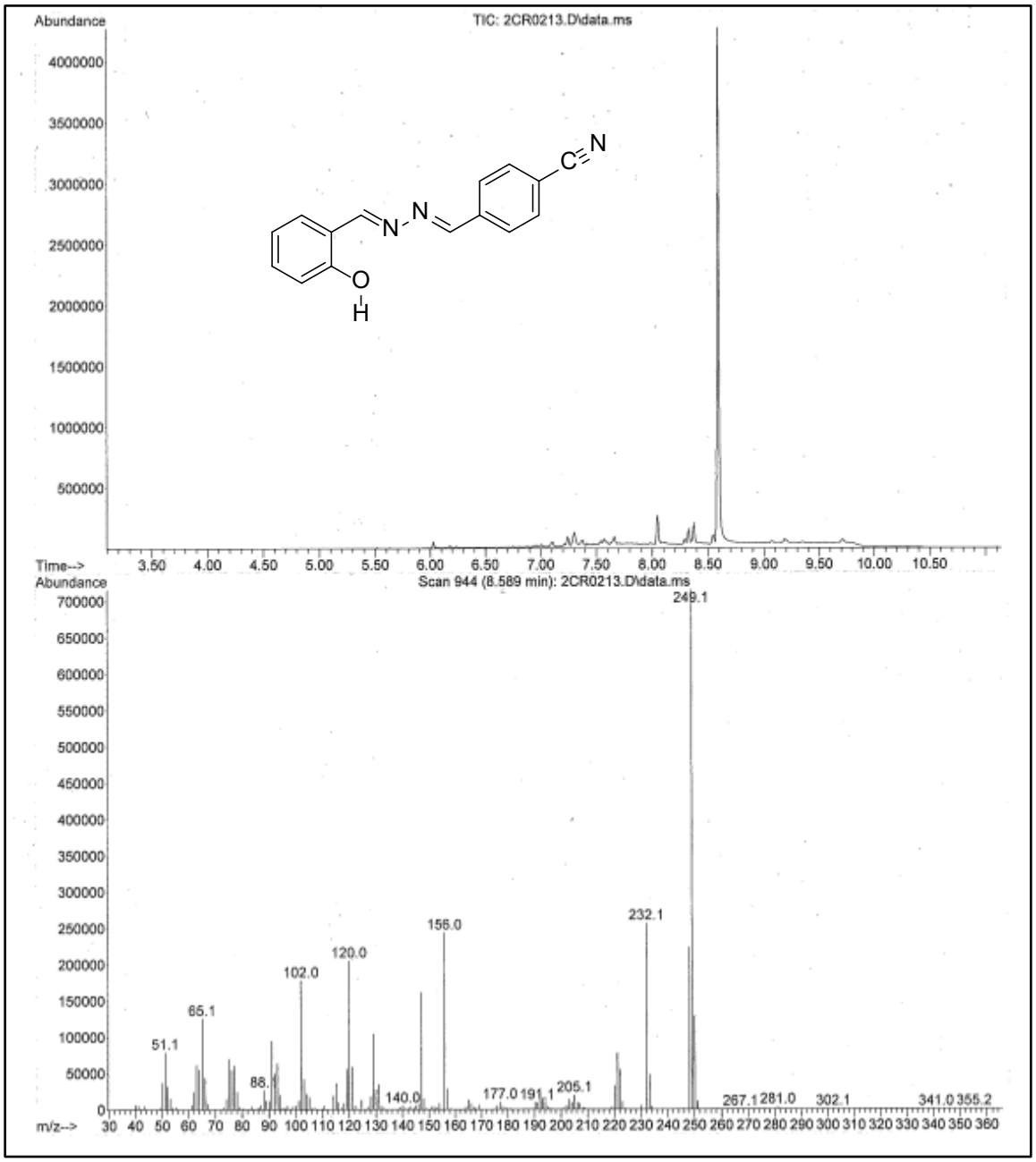
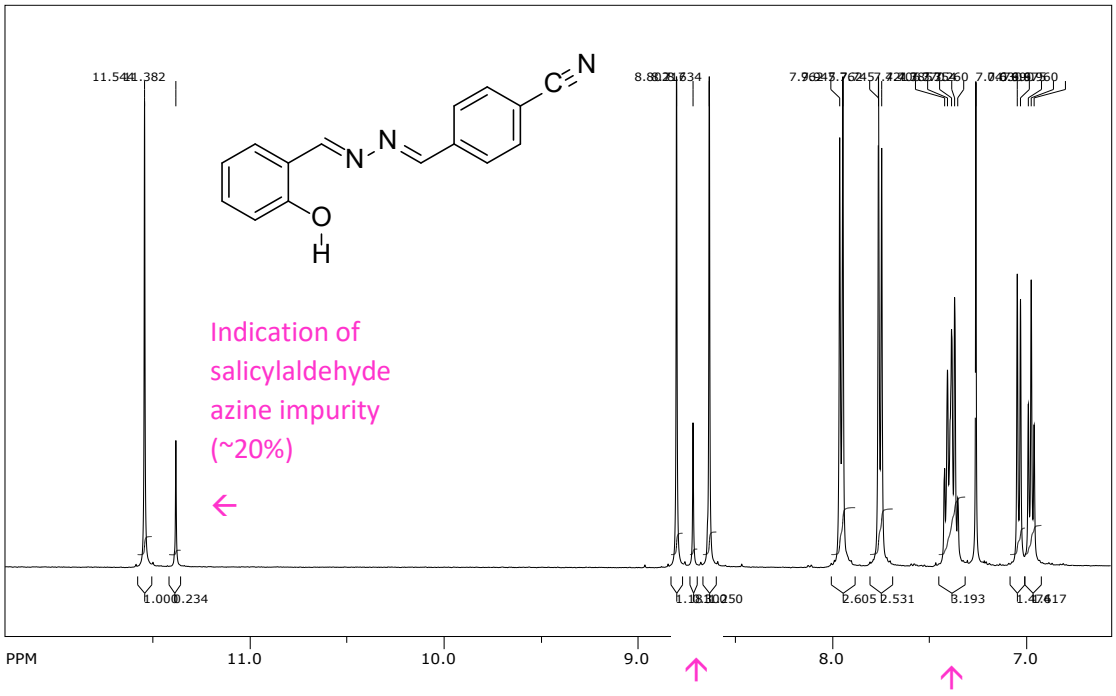


Figure 2b. ^{1}H and ^{13}C NMR of Ligand 2

^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.54 (s, 1H, O-H); 8.80 (s, 1H, H-C=N); 8.63 (s, 1H, H-C=N); 7.95 (d, 2H, J= 8.5 Hz); 7.75 (d, 2H, J= 8.5 Hz); 7.42-7.35 (m, 2H); 7.04 (d, 1H, J= 8.5 Hz); 6.98 (t, 1H, J= 7.5 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) : δ (ppm) = 166.78, 164.73, 160.04, 133.66, 133.46, 132.76, 132.60, 132.57, 128.95, 119.75, 119.71, 117.19, 117.17.



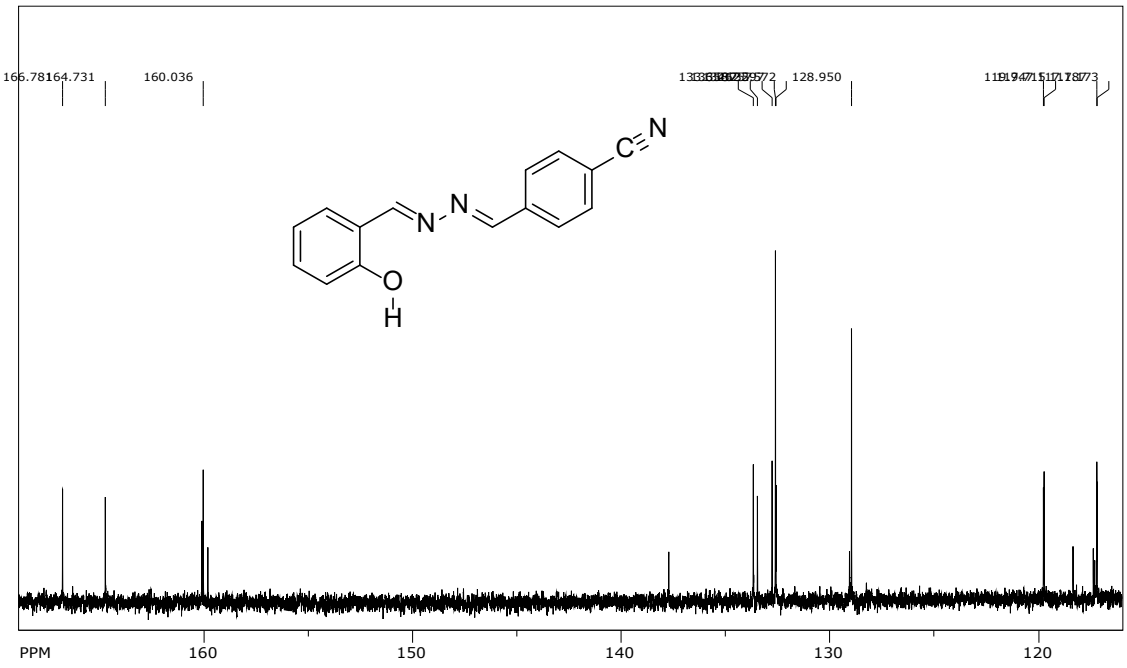


Figure 2c. Cary Fluorometer Data of Ligand 2 and Boron Complex 2
The Boron Complex 2 Intensity is recorded as is from a 3 mg sample in Ethyl Acetate in a quartz cuvette (grey). The Ligand 2 Intensity is shown x14 its actual value from a 3 mg sample in Ethyl Acetate in a quartz cuvette, so the wavelength shift could be seen in the graph (pink). Ligand 2 was excited at 423 nm, giving an emission wavelength of 528 nm. The max intensity was 17.3. Boron Complex 2 was excited at 414 nm, giving an emission wavelength of 507 nm. The max intensity was 266.7. This shows a -21 nm shift and an intensity increase by x15.4.

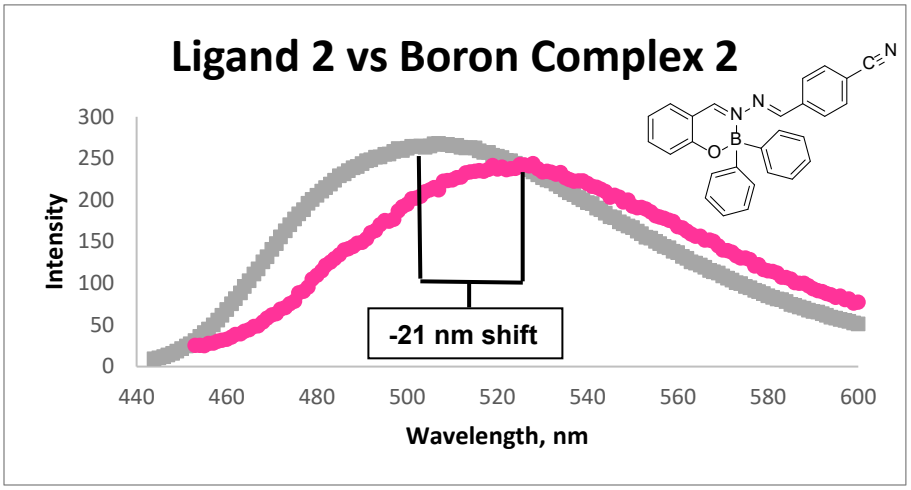


Figure 2d. ^{1}H NMR of Boron Complex 2.
The ^{1}H NMR peaks are not reported as the sample is not yet pure. It can be inferred that residual salicylaldehyde azine was present and a single boron diphenyl attached leaving the other -OH to persist at 11.55 ppm. The other -OH at 11. 39 ppm can be assumed to indicate incomplete boron diphenyl addition to the ligand. The aromatic region indicts many impurities.

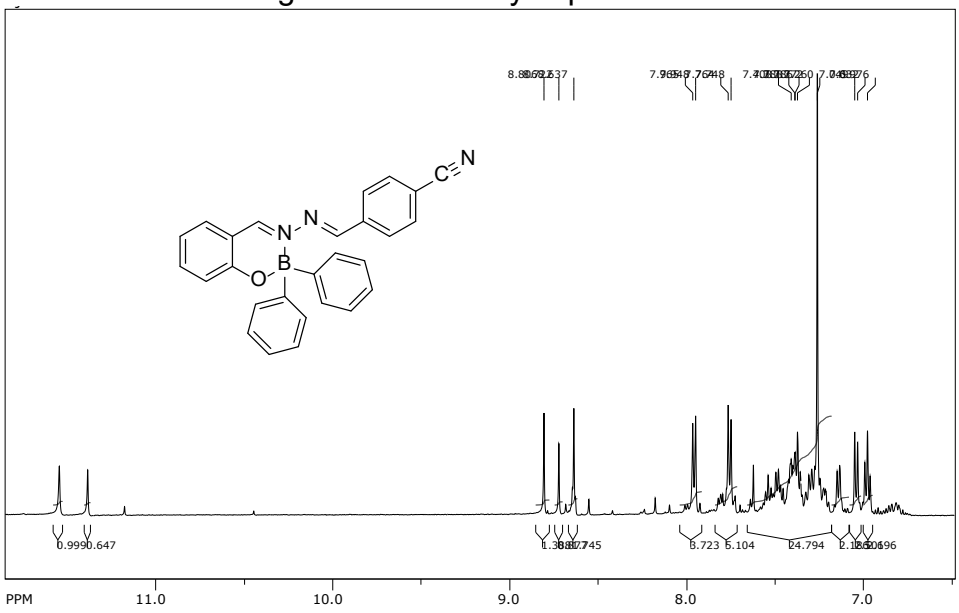


Figure 3a. GCMS Data of Ligand 3

GCMS Data shows a molecular weight of 258 g/mol as expected for Ligand 3. This agrees with its expected splitting pattern as well.

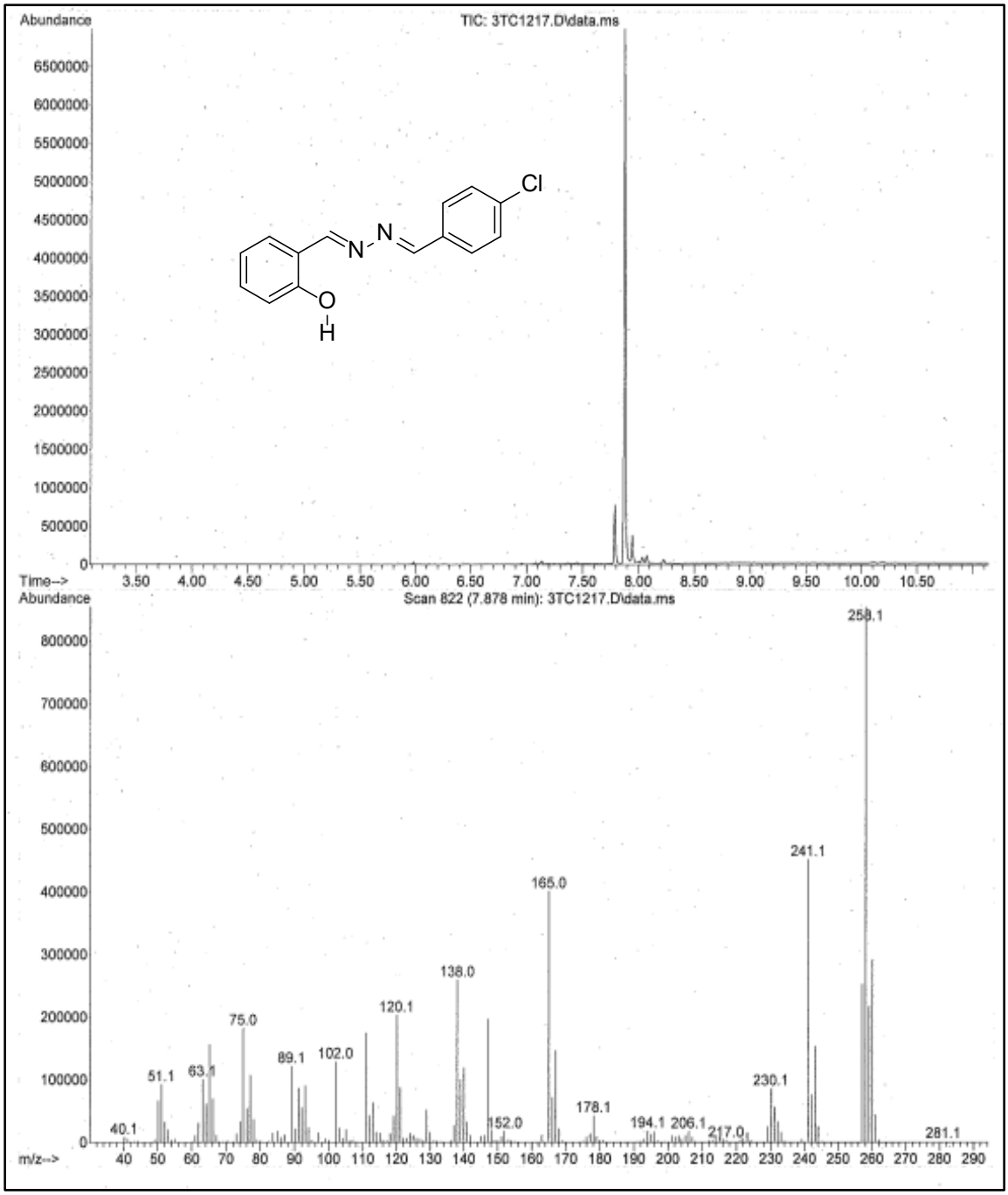
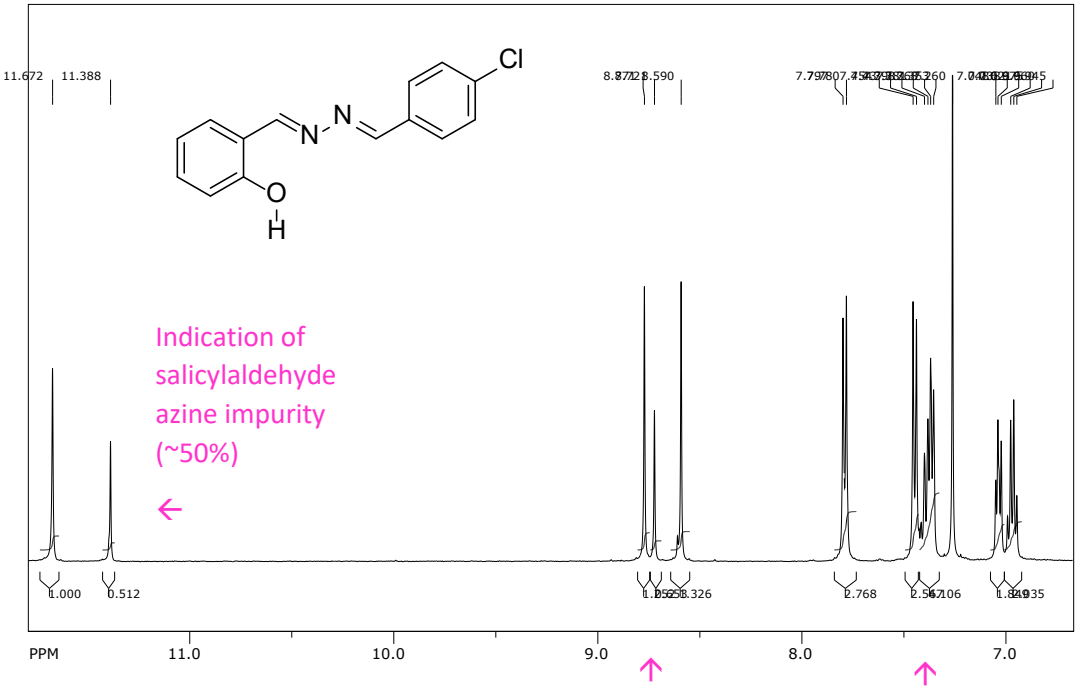


Figure 3b. ^{1}H and ^{13}C NMR of Ligand 3

^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.67 (s, 1H, O-H); 8.77 (s, 1H, H-C=N); 8.59 (s, 1H, H-C=N); 7.79 (d, 2H, J= 8.5 Hz); 7.44 (d, 2H, J= 8.5 Hz); 7.37 (m, 4H); 7.04 (m, 1H); 6.96 (t, 1H, J= 7.5 Hz). ^{13}C NMR (500 MHz, $CDCl_3$) : δ (ppm) = 165.49, 164.75, 160.96, 159.92, 133.48, 133.16, 132.48, 132.12, 129.83, 129.25, 119.58, 117.08.



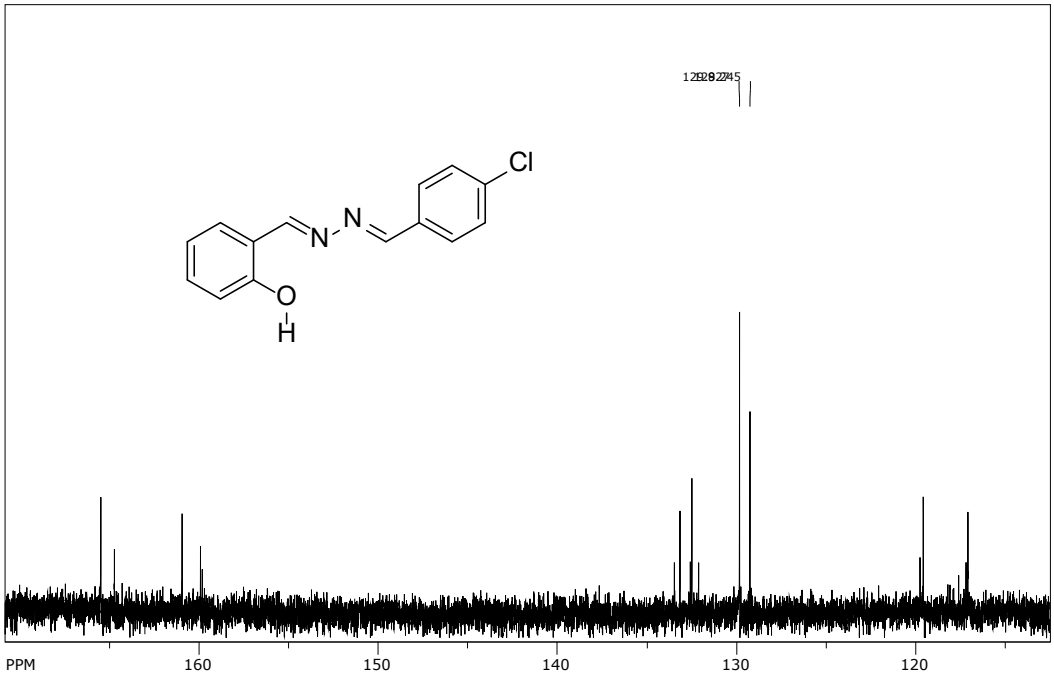


Figure 3c. Cary Fluorometer Data of Ligand 3 and Boron Complex 3
The Boron Complex 3 Intensity is recorded as is from a 3 mg sample in Ethyl Acetate in a quartz cuvette (grey). The Ligand 3 Intensity is shown x22 its actual value from a 3 mg sample in Ethyl Acetate in a quartz cuvette, so the wavelength shift could be seen in the graph (pink). Ligand 3 was excited at 414 nm, giving an emission wavelength of 490 nm. The max intensity was 17.0. Boron Complex 3 was excited at 423 nm, giving an emission wavelength of 507 nm. The max intensity was 397.1. This shows a 17 nm shift and an intensity increase by x23.4.

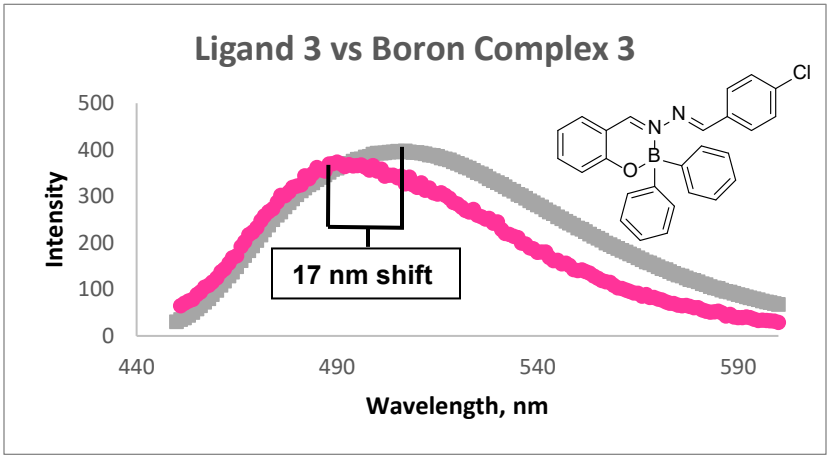


Figure 3d. ^{1}H NMR of Boron Complex 3.
The ^{1}H NMR peaks are not reported as the sample is not yet pure. It can be inferred that residual salicylaldehyde azine was present and a single boron diphenyl attached leaving the other -OH to persist at 11.67 ppm. The aromatic region indicts many impurities; however, it also is a likely sign of the boron diphenyl successfully attaching to the ligand.

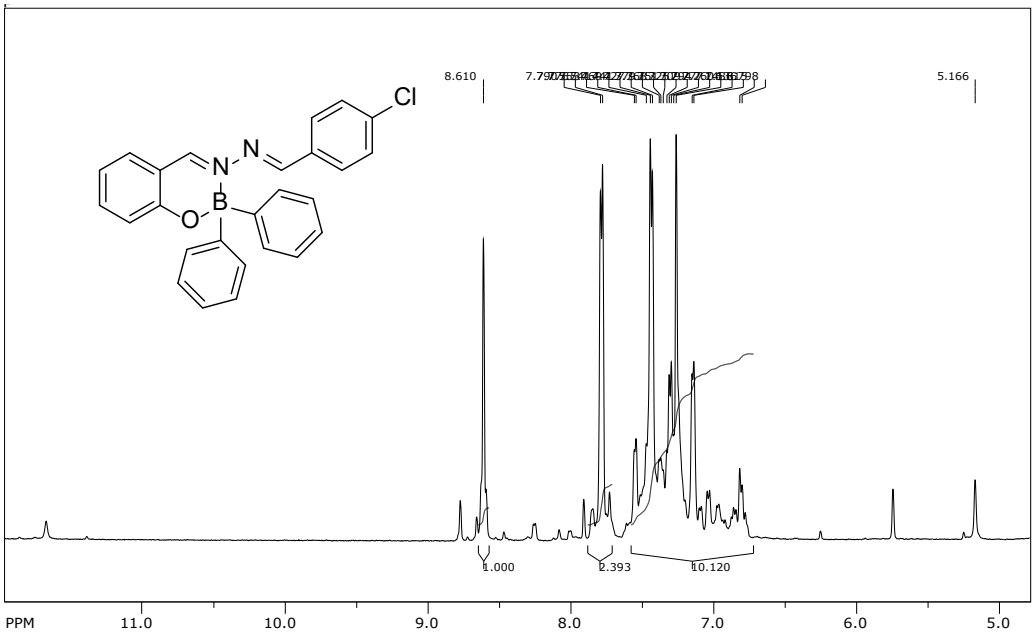


Figure 4a. GCMS Data of Ligand 4.
GCMS Data shows a molecular weight of 302 g/mol as expected for Ligand 4. This agrees with its expected splitting pattern. The double peaks associated with bromine are observed as well.

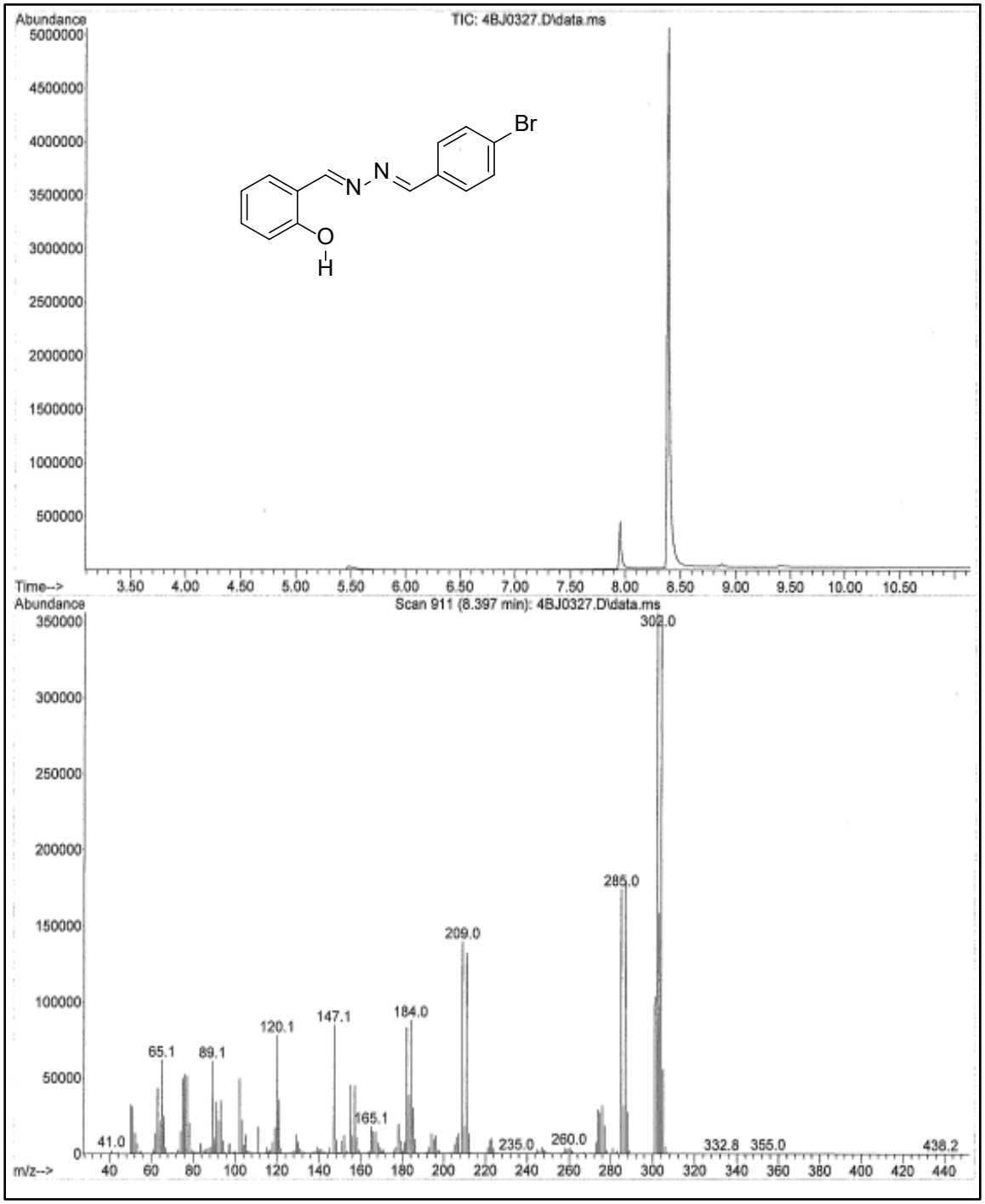


Figure 4b. ^{1}H and ^{13}C NMR of Ligand 4.
^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.66 (s, 1H, O-H); 8.77 (s, 1H, H-C=N); 8.57 (s,1H, H-C=N); 7.71 (d, 2H, J= 7.5 Hz); 7.60 (d, 2H, J= 7.5 Hz); 7.37 (m, 2H), 7.00 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) : δ (ppm) = 165.53, 164.72, 161.05, 159.91, 133.45, 133.16, 132.56, 132.49, 132.19, 132.12, 129.99, 129.94, 119.57, 117.07.

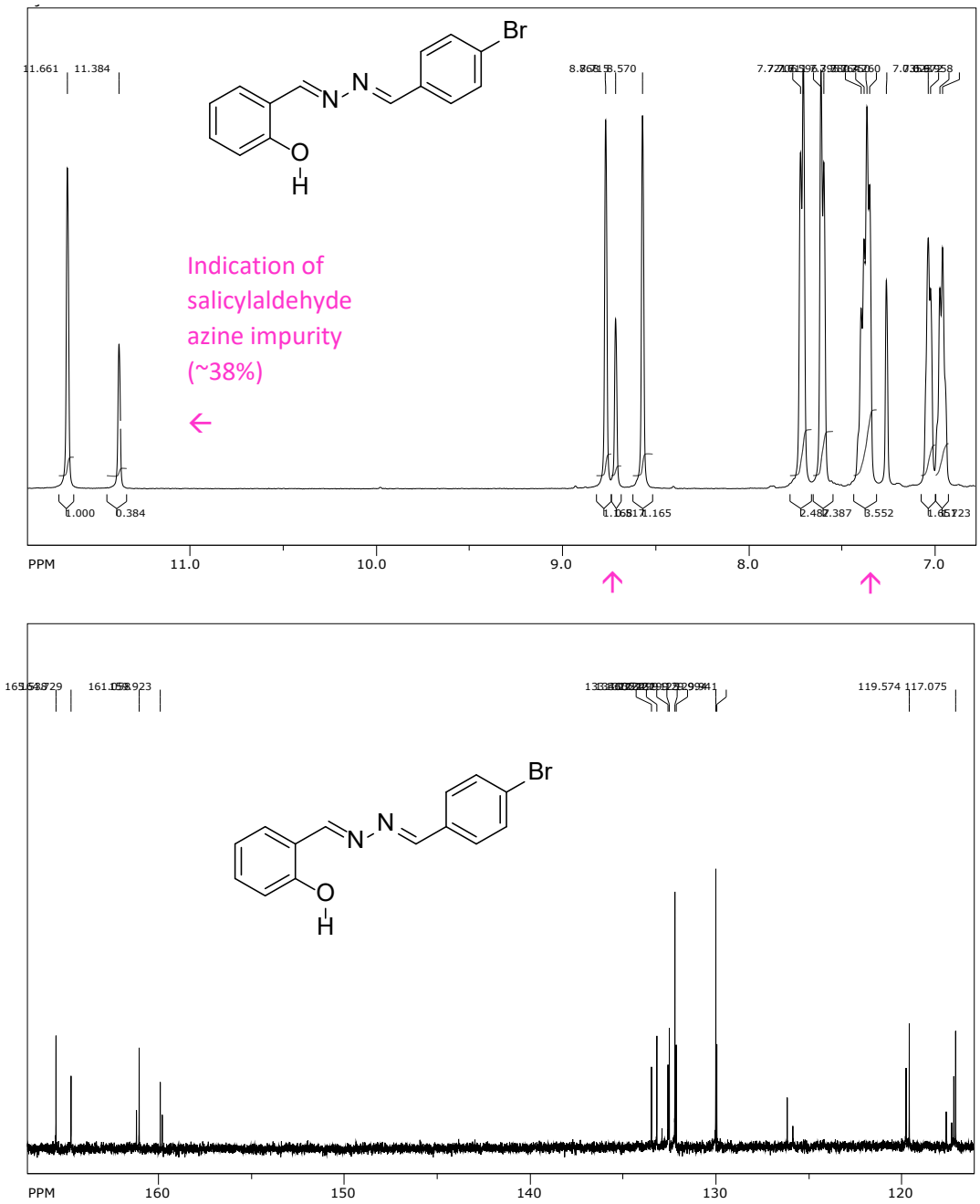


Figure 4c. Cary Fluorometer Data of Ligand 4 and Boron Complex 4
The Boron Complex 4 Intensity is recorded as is from a 3 mg sample in Ethyl Acetate in a quartz cuvette (grey). The Ligand 4 Intensity is shown x37 its actual value from a 3 mg sample in Ethyl Acetate in a quartz cuvette, so the wavelength shift could be seen in the graph (pink). Ligand 4 was excited at 426 nm, giving an emission wavelength of 502 nm. The max intensity was 16.5. Boron Complex 4 was excited at 423 nm, giving an emission wavelength of 526 nm. The max intensity was 589.2. This shows a 24 nm shift and an intensity increase by x35.7.

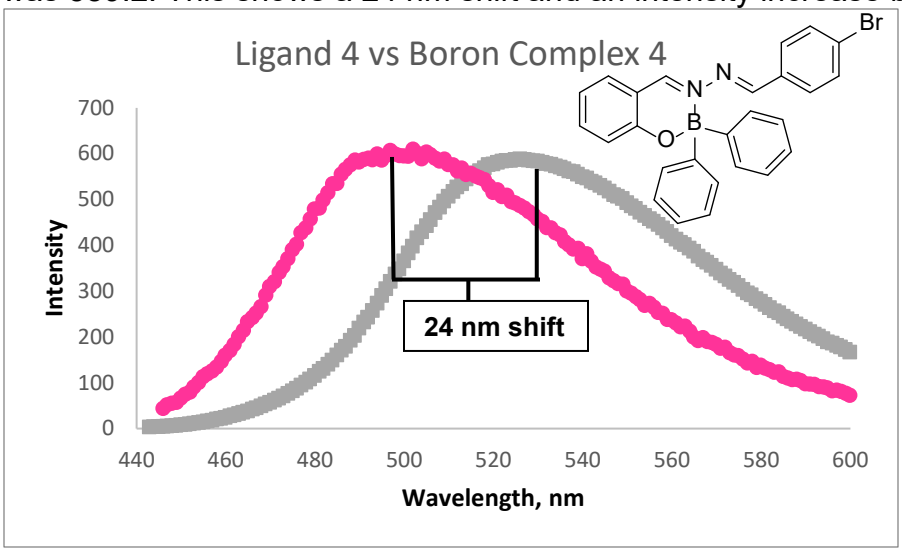


Figure 4d. ^{1}H NMR of Boron Complex 4.
The ^{1}H NMR peaks are not reported as the sample is not yet pure. It can be inferred that the boron diphenyl attached indicated by the absence of an -OH peak around 11 ppm. The aromatic region indicts many impurities; however, it also is a likely sign of the boron diphenyl successfully attaching to the ligand.

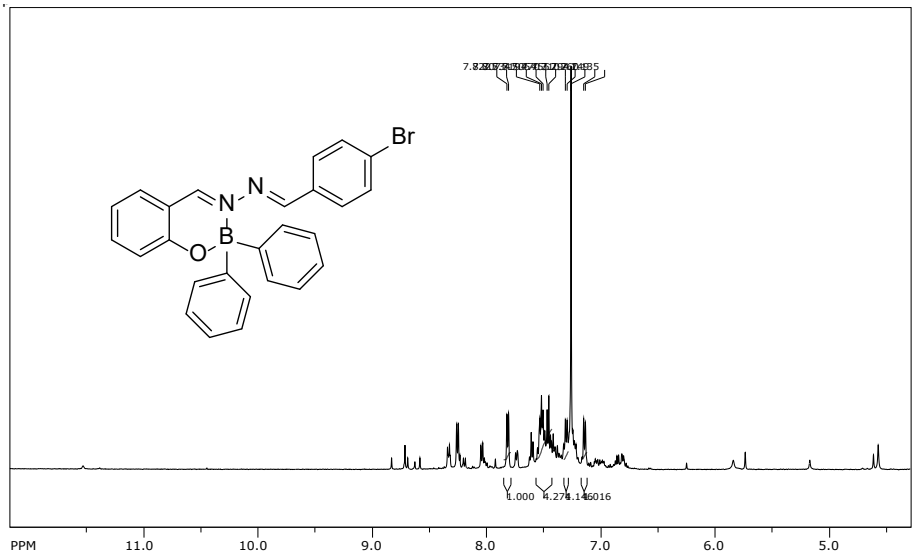


Figure 5a. GCMS Data of Ligand 5.
GCMS Data shows a molecular weight of 269 g/mol as expected for Ligand 5. This agrees with its expected splitting pattern as well.

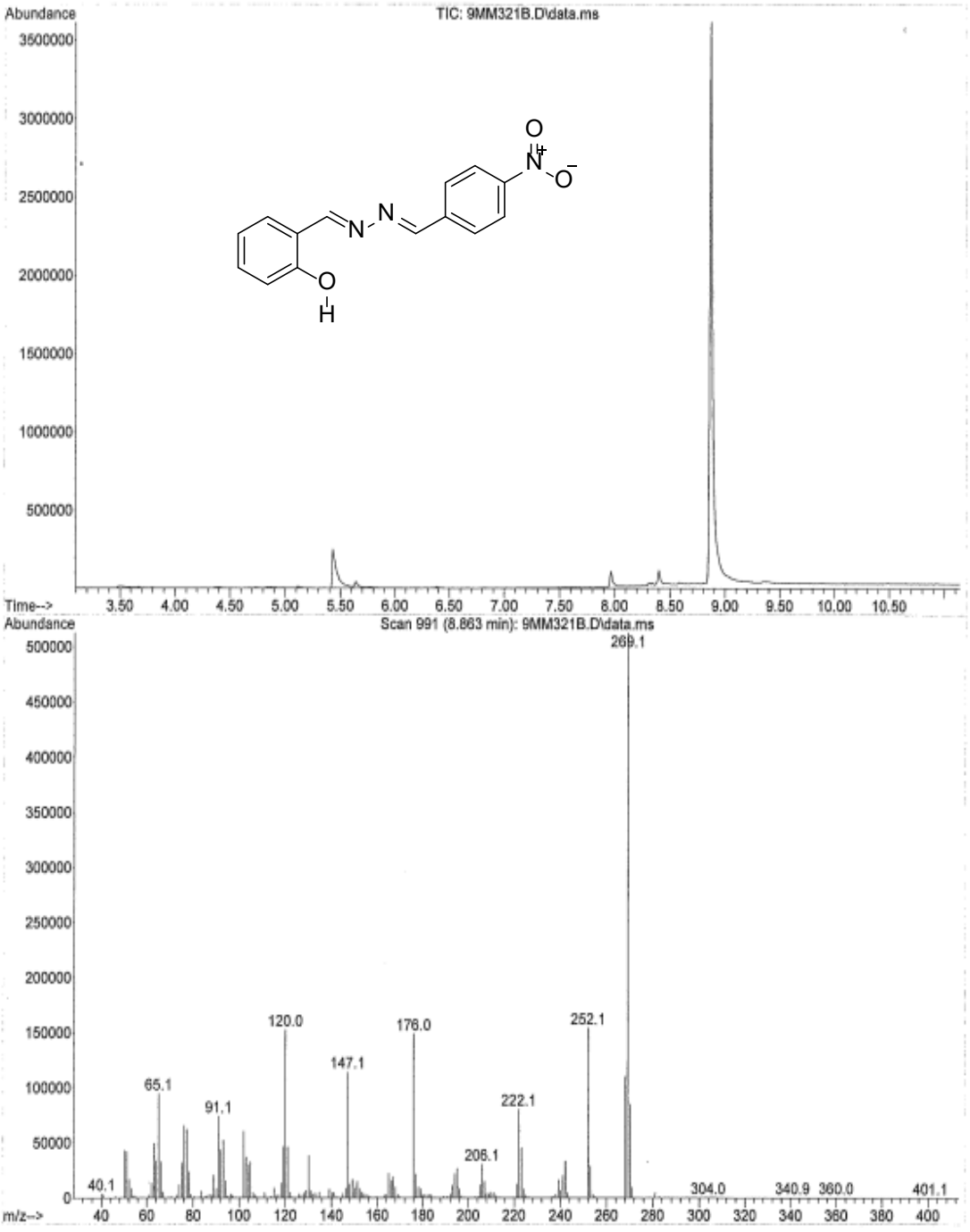
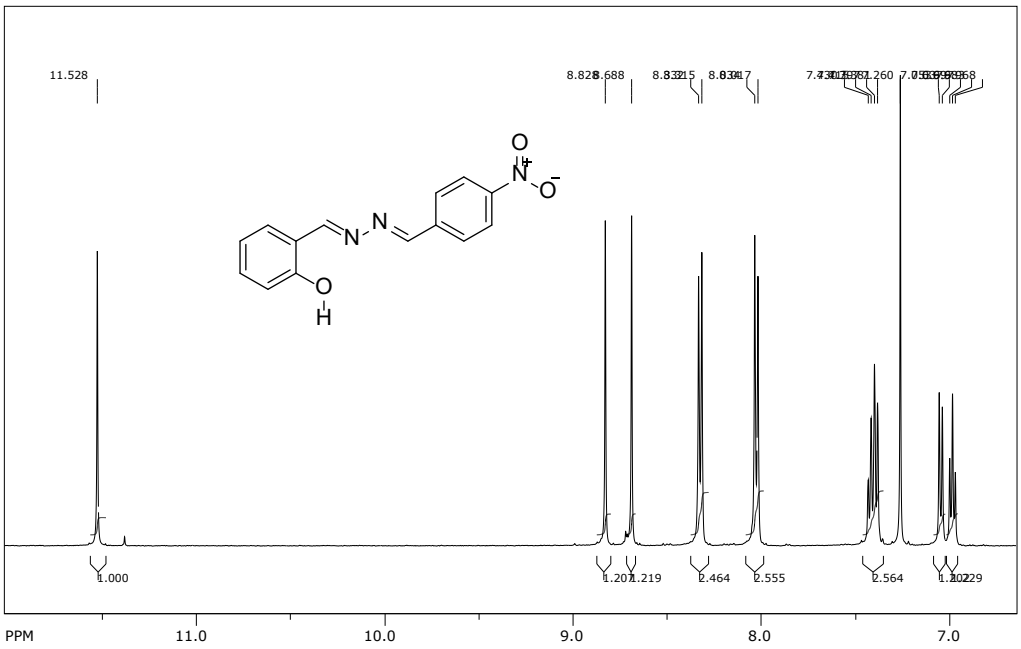


Figure 5b. ^{1}H and ^{13}C NMR of Ligand 5.

^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) = 11.53 (s, 1H, O-H); 8.83 (s, 1H, H-C=N); 8.69 (s, 1H, H-C=N); 8.32 (d, 2H, J= 8.5 Hz); 8.02 (d, 2H, J= 8.5 Hz); 7.40 (m, 2H); 7.04 (d, 1H, J= 8.0 Hz); 6.98 (t, 1H, J= 7.25 Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 167.07, 164.73, 160.15, 159.58, 139.43, 133.77, 133.45, 132.82, 132.58, 129.27, 124.10, 119.75, 117.31, 117.22.



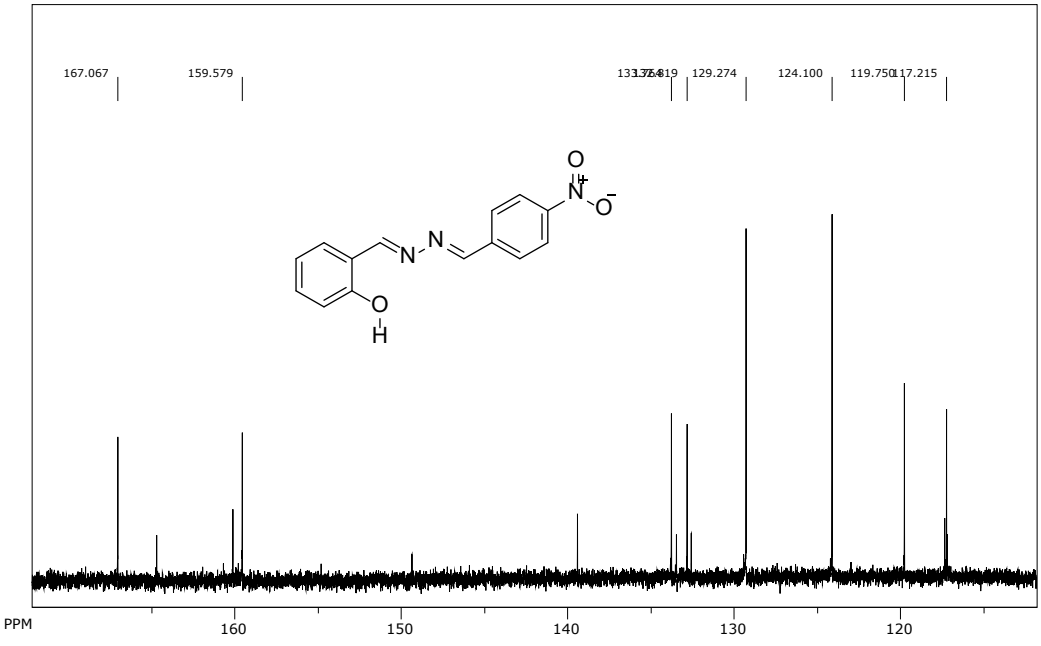


Figure 5c. Cary Fluorometer Data of Ligand 5 and Boron Complex 5
The Boron Complex 5 Intensity is recorded as is from a 1 mg sample in Ethyl Acetate in a quartz cuvette (grey). The Ligand 5 Intensity is shown x600 its actual value from a 1 mg sample in Ethyl Acetate in a quartz cuvette, so the wavelength shift could be seen in the graph (pink). Ligand 5 was excited at 416 nm, giving an emission wavelength of 610 nm. The max intensity was 0.80. Boron Complex 5 was excited at 436 nm, giving an emission wavelength of 529 nm. The max intensity was 485.0. This shows a -81 nm shift and an intensity increase by x606.3.

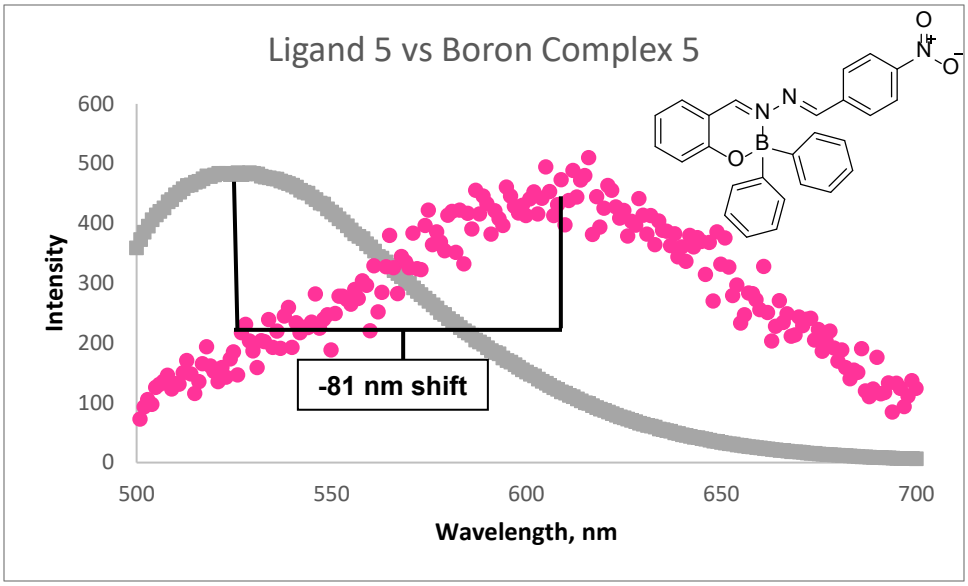
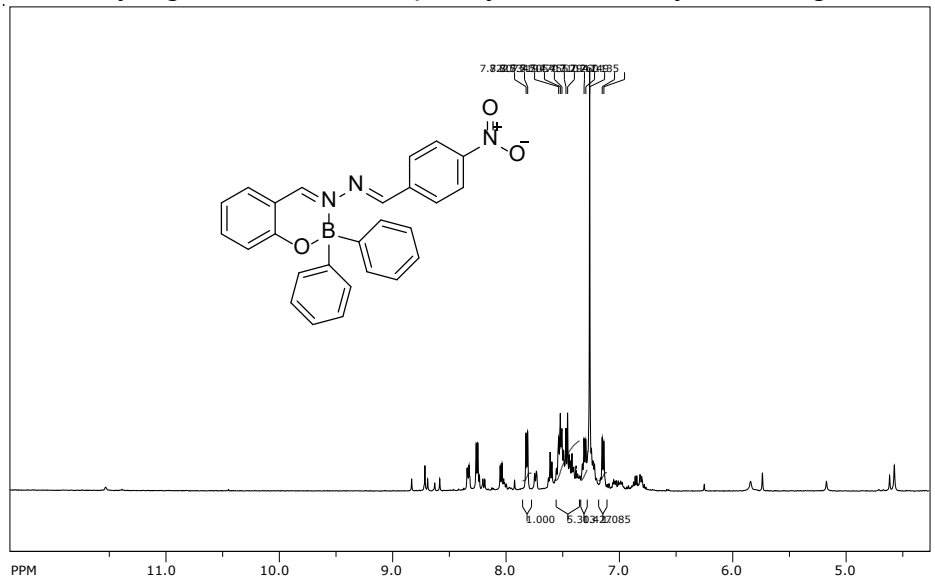


Figure 5d. ^{1}H NMR of Boron Complex 5.
The ^{1}H NMR peaks are not reported as the sample is not yet pure. It can be inferred that the boron diphenyl attached indicated by the absence of an -OH peak around 11 ppm. The aromatic region indicts many impurities; however, it also is a likely sign of the boron diphenyl successfully attaching to the ligand.



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